Review

Aqueous-phase hydrolysis of cellulose and hemicelluloses over molecular acidic catalysts: Insights into the kinetics and reaction mechanism

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ABSTRACT

The hydrolysis of cellulose and hemicelluloses in the presence of molecular acidic catalysts is of great importance for production of monosaccharides and their future utilization in bio-refinery. Moreover, the inevitable need of sustainable carbon feedstocks for fuel production and chemical industry fosters growing interest into a comprehensive understanding of this process. Hydrolysis has already been studied for many decades. Despite the high practical significance of hydrolysis, very little is known about the complex reaction networks and involved mechanisms. Meanwhile, rational process design and optimization clearly require insights into the fundamental basics of the reaction. This review summarises advances in the field of kinetic investigations aimed at understanding the hydrolysis mechanism. We consider different approaches namely (i) the simplest kinetic models; (ii) kinetic models considering oligosaccharides as intermediates; and (iii) oligosaccharides as model compounds. The contribution of these kinetic approaches to a mechanistic understanding is discussed.

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Contents

1. Introduction

Cellulose and hemicelluloses are polysaccharides that constitute 40–50 and 16–33% of the renewable feedstock lignocellulose, respectively [1]. Lignocellulose is a highly promising candidate to

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substitute fossil raw materials in future owing to several reasons. Lignocellulose is an abundant feedstock available as residue of forestry and agriculture or in form of waste streams of paper industry. Moreover, it is of great economic importance that lignocellulose is not digestible by humans; therefore, its application as feedstock does not compete with food production. Being the most attractive renewable resource, lignocellulose is extremely stable against chemical and biochemical processing due to the rigid structure of this polymeric composite.

To date, different strategies have been proposed for the valorisation of cellulose and hemicelluloses covering complete gasification, high temperature pyrolysis, as well as stepwise transformation through fractionation and depolymerisation of the lignocellulosic polysaccharides [2–4]. The latter approach offers the unique opportunity to use the high degree of functionality introduced by nature's synthesis. A potential bio-refinery scheme aiming for a controlled fractionation and depolymerisation of lignocellulose comprehends a sequence of the following steps: (1) fractionation of lignocellulose into biopolymers: cellulose, hemicelluloses and lignin; (2) depolymerisation of the biopolymers; (3) transformation of the monomers into value-added products.

Due to distinct differences of structure and reactivity of cellulose, hemicelluloses and lignin, they have to be processed under different reaction conditions [5]. A general approach toward fractionation is a selective solubilisation of lignin or hemicelluloses leaving the least-reactive cellulose intact [6]. Examples of potential fractionation processes include steam explosion for solubilisation of hemicelluloses or alkaline treatment for dissolution of lignin and partial defunctionalisation of hemicelluloses [6–8]. Fig. 1 shows examples of the integration of cellulose and hemicelluloses acid hydrolysis into the fractionation of lignocellulose.

According to the recent scientific reports, a large portfolio of chemical compounds can be synthesised based on monosaccharides [2–4]. Several carbohydrate-based processes have already been commercialised, but the majority of them relies on monosaccharides derived from edible resources such as starch or sucrose [9]. Obviously, hydrolysis of cellulose and hemicelluloses still poses challenges, which need to be solved. Different techniques can be applied for depolymerisation of polysaccharides, e.g. acid-catalysed aqueous-phase hydrolysis [10], hydrolysis using ionic liquids [11], enzymatic depolymerization [12], and solubilisation

in super-critical water with subsequent hydrolysis [13,14]. Known for a long time, acid hydrolysis of cellulose and hemicelluloses still receives great attention due to high attractiveness for commercial application. Comprehensive reviews of acid hydrolysis of polysaccharides can be found elsewhere [5,10,12,15,16]. Additionally, overviews discussing the ability of kinetic models to predict hydrolysis performance [10] or focusing on reactor and process design appeared [16]. The majority of studies considers acid hydrolysis mainly from a practical point of view, e.g. aiming for reduced process costs and gaining high yields of the products. Surprisingly, very few studies target fundamental insights into the mechanism of hydrolysis on a molecular level. However, one can expect a very complicated reaction network, taking into account the complexity of the substrates and the high reactivity of the products. Nevertheless, the detailed knowledge on the mechanism and kinetics of hydrolysis are essential for process design and optimizing the catalytic performance.

In this review, we summarise the insights gained into the reaction mechanisms via kinetic investigations of cellulose and hemicelluloses hydrolysis. As catalytic activity of solid acid catalysts for hydrolysis of cellulose [17] and oligosaccharides [18] has very recently been reviewed, we herein focus on soluble acids. In Section 2 of this review, the structures of cellulose and hemicelluloses are considered. Section 3 overviews the reaction conditions of hydrolysis. The conventional models for hydrolysis, which only account for substrates and final products, are described in Section 4. The progress in kinetic modeling by integration of intermediates is summarised in Section 5. The final Section 6 summarises differences in the reactivity of oligosaccharides with defined chain lengths as substrates.
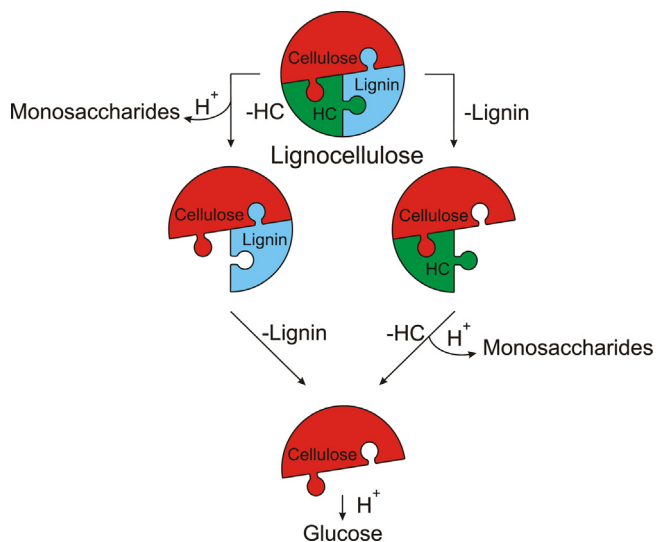
2. Structure of cellulose and hemicelluloses

Cellulose is the most abundant homopolysaccharide in nature representing about 1.5×10^{12} tons of the annual biomass production. The cellulose macromolecule is composed of D-glucose monomer units connected to each other via β-1,4-glycosidic bonds (Fig. 2).

The degree of polymerization of cellulose is dependent on the cellulose source. Cellulose chains in primary plant cell walls, have a degree of polymerisation (DP) ranging from 5000 to 7500 glucose units, and in wood and cotton-based materials between 10,000 and 15,000 [19].

Each repeating unit of cellulose contains three hydroxyl groups which are involved in networking of the units with hydrogen bonds (Fig. 2). The intra-chain hydrogen bonding between hydroxyl groups and oxygen of the adjacent ring molecules makes the linkage stable and results in the linear configuration of the cellulose chains [20].

The cellulose structure consists of crystalline and amorphous domains. The hydroxyl groups in cellulose chains form intra- and intermolecular hydrogen bonds constituting the crystalline structure. The crystalline structure of cellulose can be classified into seven allomorphic forms denoted as cellulose I_α, I_β, II, III_I III_{II}, IV_I, IV_{II}. Celluloses I_α, and I_β are the major crystal forms in nature and

Fig. 1. Examples of cellulose and hemicelluloses acid hydrolysis integration into fractionation of lignocellulose. HC denotes hemicelluloses. Monosaccharides denote products of hemicellulose hydrolysis [6–8].
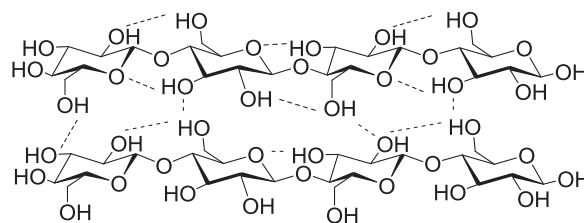
Fig. 2. Schematic structure of cellulose.

are also known as native cellulose. Among all forms, cellulose II is the most thermodynamically stable. It can be formed from celluloses I_α, and I_β by treatment with aqueous sodium hydroxide or through dissolution of cellulose and subsequent regeneration [20]. The arrangement of cellulose molecules with respect to each other and to the fiber axis determines the physical and chemical properties of cellulose. The fiber structure of cellulose provides its high chemical stability. Crystalline domains of cellulose are less accessible to chemical reactants. On the other hand, amorphous regions are easily penetrated by reactants during chemical reactions [20]. The reactivity of cellulose can be determined by several factors such as hydrogen bonding, the length of chains, the distribution of chain length, the crystallinity and the distribution of functional groups within the repeating units and along the polymer chains [19].

Hemicelluloses are the second major polysaccharides in plant cell. Unlike cellulose, hemicelluloses are heteropolymers, i.e. they are composed of different monomeric units. Hemicelluloses are often branched: they have a main chain and side groups attached to it. A number of monosaccharides and organic acids can be produced by hydrolysis of hemicelluloses, e.g. xylose, arabinose, mannose, galactose, acetic acid, glucuronic acid, etc. Table 1 illustrates the structural formulae of hemicelluloses.

Hydrolysis of xylose-containing hemicelluloses called xylans is the most studied system to date due to high availability of these polysaccharides from herbaceous plants and hardwoods. Xylans have a β-(1->4)-D-xylopyranose backbone with side residues that vary depending on the source of xylan. Herbaceous plants contain high amounts of arabinoxylan. Therein, C_2 and C_3 hydroxyls of β-(1->4)-D-xylopyranose in the backbone are connected with L-arabinofuranosyl residues linked via α-(1->2,3) bonds (Table 1). Arabinoxylans are highly branched polysaccharides with a molar ratio arabinose/xylose between 0.5 and 1 [15,21]. Hardwood xylan, acetyl-4-O-methylglucuronoxylan, has 4-O-methyl-α-D-glucopyranosyluronic acid and acetyl residues attached to C_2 and C_3 hydroxyls. The molar ratio of xylose/glucuronic acid/acetyl residues is about 10:1:7 [12]. Being the predominating hemicelluloses in herbaceous and hardwoods, xylans comprise only 7–10% of the dry weight of softwood biomass. Softwood xylans, arabino-4-O-methylglucuronoxylans, are not acetylated but the xylan backbone is substituted at carbons 2 and 3 with 4-O-methyl-α-D-glucuronic acid and α-L-arabinofuranosyl residues, respectively [12]. In softwood xylans, the molar ratio of xylose/glucuronic acid/arabinose is about 8:1.6:1 to 10:2:1 [12].

Galactoglucomannans (Table 1) with 15–20% dry weight prevail in softwood. The backbone of galactoglucomannans consists of β-(1->4)-linked β-D-mannopyranosyls and β-D-glucopyranosyls. The units are partially acetylated in C_2 and C_3 positions and bear α-D-galactopyranose units attached to C_6 [22]. Galactoglucomannans can be fractionised into water and alkaline-soluble sub-types that differ in composition. The ratios of mannose/glucose/galactose/acetyl residues are 3:1:1:0.24 for the water-soluble fraction and 3:1:0.1:0.24 for the alkali-soluble fraction [12].

Arabinogalactan (Table 1) is a polysaccharide that is present mainly in the heartwood of the genus Larix and is available as a minor water-soluble component of softwoods. As arabinogalactan is located in the lumen of the tracheids and ray cells, it is not a cell-wall component and is not by definition a true hemicellulose [23]. However, arabinogalactan is often assigned to hemicelluloses by the investigators in the field of wood and pulping research [23], as well as hydrolysis [24,25], and therefore is considered here. The main chain of arabinogalactan consists of β-(1->3)-linked β-D-galactopyranosyl units, the majority of which carries residues attached to the C_6 position. The residues linked with the main chain are monomers or oligomers (in most cases dimers) of β-D-galactopyranosyl units. Alternatively, arabinose as single α-

arabinofuranosyl or dimeric side chain is attached to the C_6 position of the units in the main chain [23]. Commonly, arabinogalactans exhibit a molar ratio of galactose/arabinose of 6:1 [12,15,23]. Additionally, arabinogalactan contains small amounts of glucuronic acid residues incorporated in the side chains [23]. Noteworthy, the arabinogalactan discussed herein should not be mixed up with another polymer that has a linear bond of β-(1->4)-linked β-D-galactopyranosyl units and bears α-L-arabinofuranosic residues at position C_3. The latter polymer is also referred to as "arabinogalactan" in literature and is commonly found in pectins from citrus, apple and potato [23].

Importantly, the sub-class and polymerisation degree of hemicelluloses depends on not only the plant species, but also the tissue type and development stage [12,26]. Hemicelluloses were reported to be chemically associated with lignin, cellulose or proteins [12]. Spectroscopic data suggest that most probably hemicelluloses are not connected to cellulose via chemical bonding, but rather via hydrogen bonds or van der Waals forces [12]. On the contrary, chemical association of hemicelluloses with phenolic lignin compounds has been known for a long time. For example, ferulic or *p*-coumaric acids form covalent bonds to side chain residues of xylans. 4-O-methyl-α-D-glucuronic and L-arabinofuranosyl residues are attached to lignin via ester and ether bonds, respectively [12,22]. As shown below, such chemical association is considered as a reason for existence of slow-reacting xylan. Alike cellulose, backbones of hemicelluloses consist of β-(1->4)-linked monomers, but the branched structure of hemicelluloses prevents extensive formation of hydrogen bonds. Hence, in contrast to cellulose, hemicelluloses are amorphous, and therefore exhibit higher reactivity for hydrolysis. Hemicelluloses are not soluble in water at room temperature, but they can be solubilized in hot water or aqueous solutions. For instance, a well-established method for isolation of arabinogalactan is extraction with hot water [22,23]. Hardwood xylan can be isolated when extracting with an aqueous solution of NaOH after delignification of wood [22,23]. Galactoglucomannan is extractable with a sodium hydroxide solution containing borates [22].

3. Reaction conditions of hydrolysis

One of the attempts to utilize the polysaccharides comprising lignocellulose considered the treatment of wood with an acid to conduct simultaneous hydrolysis of hemicelluloses and cellulose [5]. However, amorphous hemicelluloses undergo hydrolysis under milder conditions than crystalline cellulose. In addition, under the harsh reaction conditions required for acid hydrolysis of cellulose, monosaccharides derived from hemicelluloses suffer from decomposition (Fig. 3). Elaboration of two-step processes improved the overall yield of derived monosaccharides [5]. The first step of such processes is treatment of wood with diluted acids under mild conditions to accomplish hydrolysis of hemicelluloses leaving solid cellulose and lignin unaltered. Dissolved hemicellulosic monosaccharides can be easily isolated with the liquid phase. The second step of the process is hydrolysis of cellulose under harsher conditions. Processes for "wood saccharification" are known for a long time including examples such as the two-step Scholler process or the Noguchi process [15].

3.1. Cellulose

Hydrolysis of cellulose with dilute or concentrated sulfuric acid and HCl has been used since the 1940s [29–31]. Two different methods have been applied for acid hydrolysis of cellulose. The first method uses a high concentration of mineral acids (e.g., 15–16 N HCl or 31–70 wt% H_2SO_4) and low operation temperatures

(20–50 °C). The major drawbacks of this method are the high cost of acid recovery and the need for expensive construction materials. In the second method, a highly diluted acid (pH 1.5–2.5) at high operation temperatures (200–230 °C) is utilised. This method is more favorable and most frequently applied [27,28].

Reaction conditions dramatically influence the yield of glucose. An optimisation of reaction parameters requires considering conditions such as reaction time, initial concentration, reactor configuration (CSTR, plug flow, percolation reactor), operation mode (batch, continuous), the applied temperature and acid concentration. For example, the yield of glucose was about 50% when using a plug flow reactor with short residence time of 0.22 min and 1 wt.% of sulfuric acid at 240 °C. In batch operation with 0.07 wt.% of sulfuric acid, 65% yield of glucose could be obtained after 30 min. It should be noted that harsh reaction conditions, i.e. high temperature and long time, lead to enhanced degradation to dehydration products including HMF, furfural and levulinic acid. Due to the presence of minerals in cellulose, partial neutralisation of acidic catalysts takes place [32–34]. Therefore, several investigators proposed including the neutralization capacity of cellulose into the rate of hydrolysis [35,36].

3.2. Hemicelluloses

For the recent 20–30 years, the attention to acid hydrolysis of hemicellulosic components of lignocellulose has increased. This development is connected with novel "bio-refinery concepts" and growing interest in microbial synthesis of bioethanol [10]. Switching from a starch-, sucrose- and glucose-based production of bioethanol to lignocellulosic bioethanol is very beneficial from an economical point. However, cellulose as a part of lignocellulose is strongly associated with lignin and hemicelluloses dramatically hampering the access of microorganisms to cellulose [10,12]. The accessibility of cellulose can be increased by treating lignocellulose with diluted acids [10,12]. Efficient removal of hemicelluloses prior to fermentation is crucial, because the cellulase

Table 1
Structural formulae, composition and plant source of hemicelluloses. Abbreviations: Xyl is xylose, Ara is arabinose, GluA is glucuronic acid, Ac is acetyl, Man is mannose, Gal is galactose.
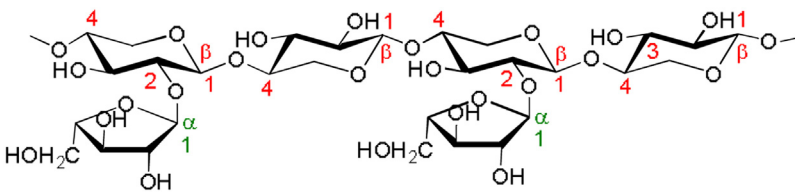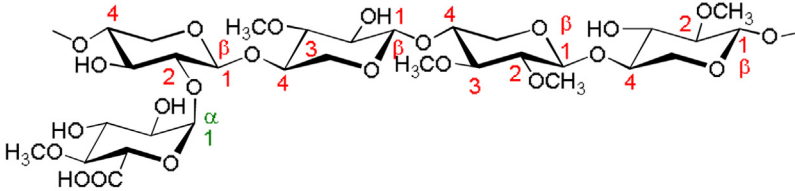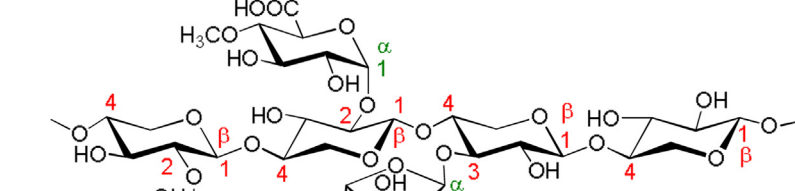
Type	Structural formula	Composition	Plant source
Arabinoxylan		Xyl:Ara 1:0.5 to 1:1	Herbaceous plants
Acetyl-4-O-methylglucuronoxylan		Xyl:GluA:Ac 10:1:7	Hardwoods
Arabino-4-O-methylglucuronoxylan		Xyl:GluA:Ara 8:1.6:1 to 10:2:1	Softwoods

Table 1 (*Continued*)

Type	Structural formula	Composition	Plant source
Galactoglucomannan		Man:Glu:Gal:Ac 3:1:1:0.24 (water-soluble) or 3:1:0.1:0.24 (alkali-soluble)	Softwoods
Arabinogalactan		Gal:Ara 6:1	Softwoods

→ 4-β-D-Man p-1 → 4-β-D-Man p-1 → 4-β-D-Glu p-1 → 4-β-D-Man p-
3   6   1   2
↑   ↑   ↑
Ac   1   Ac
                                                    α-D-Gal f

→ 3-β-D-Gal p-1 → 3-β-D-Gal p-1 → 3-β-D-Gal p-1 → 3-β-D-Gal p-1 →
6   6   6   6
↑   ↑   ↑   ↑
1   1   1   1
β-D-Gal p   α-L-Ara f   β-D-Gal p   α-L-Ara f
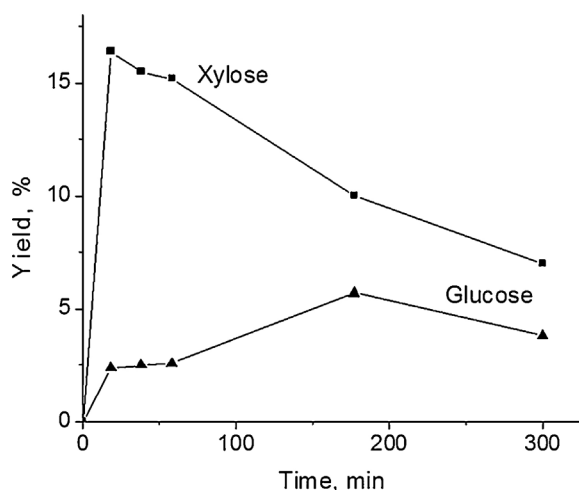6
↑
1
β-D-Gal p

Fig. 3. Release of xylose (squares) and glucose (triangles) during hydrolysis of sugar cane bagasse catalyzed by 2% H_2SO_4 at 128 °C [65].

enzyme is significantly inhibited by xylose, xylan and especially xylo-oligosaccharides [37,38,39].

In this case, the process can be considered both as a pre-treatment technique and as a way to recover hemicellulosic monosaccharides [5]. Therefore, such approaches are sometimes referred to as "acid pre-hydrolysis".

Acid pre-hydrolysis of lignocellulose is carried out in the presence of diluted acids with a concentration of 0.25–6 wt.% [40–50]. Investigations mainly focus on H_2SO_4[40–45,47,48,50] as catalyst, but other mineral acids such as HCl, [24,45,46,51], H_3PO_4[52], or HNO_3[46], and organic acids, e.g. maleic [53,54], oxalic [54,55], acetic [56] or trifluroacetic acids [55] were also tested. At pH 2 and lower, the rate of hydrolysis is a function of proton concentration and does not depend on the nature of the acid catalyst [54,55].

The reaction is usually conducted in a temperature range of 70 to 220 °C [24,40–45,47–50]. At low temperatures, hydrolysis is too slow, while at high temperature, also cellulose starts to hydrolyse. Many efforts were made preventing monosaccharide decomposition. A high selectivity toward monosaccharides is crucial, as side products such as furfural inhibit subsequent fermentation [10]. Hydrolysis at high temperature is often complete within less than 2 h [40,41,43–48,50] but is associated with the mentioned by-products formation [44–46,50,54,57]. Lowering the temperature to 90 °C increases selectivity to 100%. However, up to 24 h are required for full conversion of hemicelluloses under these conditions [24,40,42,55]. Acid pre-treatments aim at a selective hydrolysis of hemicelluloses, but lignocellulose contains minerals that are washed out resulting in partial neutralisation of the acid [41,43,50,54,56,58]. For instance, when working with 0.2% H_2SO_4

at low liquid to solid ratio, Cahela et al. reported neutralisation of up to 70% of the acid upon pre-hydrolysis [59]. Moreover, dissolution of some parts of lignin [45,49,60] and cellulose [41,61] has been reported. An example adopted from [65] is shown in Fig. 3 to illustrate the described effect. Hydrolysis of sugar cane bagasse in the presence of sulfuric acid was studied and mainly hydrolysis of xylan to xylose was observed. However, prolonging the reaction resulted in decomposition of xylose along with some degradation of cellulose to glucose.

Minor amounts of glucose appear sometimes among the products of pre-treatments [45,49–51,61]. Typically, it is difficult to detect if glucose results from hydrolysis of hemicelluloses or cellulose. Nevertheless, Marcotullio et al. concluded that cellulose is hardly affected by a pre-treatment with HCl based on thermogravimetric and X-ray diffraction analyses of the solid residues after treatment [51]. Optimisation of reaction conditions enables hydrolysis of hemicellulose with yields above 70% [43–45,49,50] sometimes even reaching 96–98% (Fig. 4) [51,53,54]. Although a comprehensive economic analysis is out of the scope of this review, the major challenge caused by low concentrations of monosaccharides requires attention. In the best case, a hydrolysate of hemicelluloses contains $20\,\mathrm{g\,L^{-1}}$ monosaccharides [42,46,53], i.e. 2 wt.%, which is too low for profitable processing.

Hydrolysis of hemicelluloses using pure water is also the focus of numerous investigations [54,60,62–64]. The main motivation for using non-acid aqueous hydrolysis is exclusion of soluble acids. Although diluted sulfuric acid is an extremely cheap reagent, its exploitation dramatically increases the capital costs, as it requires a corrosion resistant construction [10]. Furthermore, classic removal of sulfuric acid from monosaccharide hydrolysates proceeds via precipitation with calcium ions. Consequently, lime is produced as side product and needs disposal. Aqueous hydrolysis can be performed as e.g. treatment of lignocellulose with hot water or applying steam explosion [5,7]. The process is usually conducted at 150–220 °C [5,49,54,60,62–68,66], i.e. it requires higher temperatures compared to acid hydrolysis. Partial delignification [54,60] as well as some degradation of the soluble products to furfural [67,68] is typical of auto-hydrolysis. The active species for catalysis are proposed to form by auto-protolysis of water at high temperatures. Indeed, the H_3O^+ and OH^- concentration rises form $1\cdot10^{-7}\,\mathrm{mol\,L^{-1}}$ (pH 7) at room temperature to ca. $3.2\cdot10^{-6}\,\mathrm{mol\,L^{-1}}$ (pH 5.6) at 220 °C [69]. Additionally, high temperature treatments with water result in release of acetic acid, which is a component of many hemicelluloses (Table 1), thereby accelerating hydrolysis. Unlike acid hydrolysis, the main soluble product of aqueous hydrolysis is a mixture of oligosaccharides (Fig. 4). The portion of monosaccharides does usually not exceed 10% and the overall yield of products is limited to ca. 70–80% [49,54,60].

An alternative approach toward valorisation of hemicelluloses concerns a two-step hydrolysis that includes (i) isolation of hemicelluloses and (ii) acid hydrolysis, respectively [24,55]. This two-step process helps to avoid the aforementioned side processes, e.g. dissolution of lignin or hydrolysis of cellulose. The hydrolysis kinetics of isolated and non-isolated hemicelluloses exhibits some differences that will be discussed in the following sections.

4. Conventional kinetic model

4.1. Cellulose

Kinetics of polysaccharide hydrolysis, especially for cellulose, has been widely studied. The simplest kinetic models for hydrolysis of polysaccharides do not consider any intermediates, but only the final products of the reaction and sometimes the substrate. The

majority of kinetic studies proposes a lumped model in which the polymer and all oligomers are treated as one substrate.

One of the first systematic kinetic studies on biomass hydrolysis was reported by Saeman in 1945 [29]. Hydrolysis of cellulose was assumed to be pseudo homogeneous first order and to follow two consecutive reactions (Eq. (1)):

$$\mathrm{Cellulose} \overset{k_1}{\rightarrow} \mathrm{Glucose} \overset{k_2}{\rightarrow} \mathrm{Degradation \quad products} \tag{1}$$
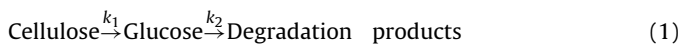
The following reaction rate equations were used describing cellulose and glucose concentrations:

$$\frac{d\,[\mathrm{cellulose}]}{dt} = -k_1\,[\mathrm{cellulose}] \tag{2}$$

$$\frac{d\,[\mathrm{glucose}]}{dt} = k_1\,[\mathrm{cellulose}] - k_2\,[\mathrm{glucose}] \tag{3}$$

As cellulose is insoluble in water, Saeman's model includes the residual mass of cellulose determined gravimetrically [29]. The reaction rate constants k_i follow Arrhenius temperature dependence including acid concentration as shown in Eq. (4),

$$k_i = k_{0,i}[A]^m e^{\frac{-E_a}{RT}} \tag{4}$$

where $k_{(0,i)}$ is the pre-exponential factor, [A] is the acid concentration, and m is an empirical exponent.

The model proposed by Saeman for hydrolysis of cellulose (Eq. (1)) has also been applied frequently to describe hydrolysis of hemicelluloses [24,42,48,50,68,70]. A literature overview of kinetics of acid hydrolysis of polysaccharides at different acid concentrations and temperatures is presented in Table 2. The apparent activation energies of different sources of cellulose vary in a broad range of 105–$188\,\mathrm{kJ\,mol^{-1}}$. For example, higher activation energies have been determined for Kraft and filter paper, whereas lower ones are obtained for sugarcane and wheat straw. This indicates that such a simple kinetic model of hydrolysis cannot be applied on the entire range of reaction temperatures and acid concentrations.

These variations in kinetic parameters could be explained by factors such as the heterogeneous nature of different substrates, diffusion limitations in the early state of hydrolysis or changes of the physical structure of the substrate during hydrolysis [27,71].

Somewhat earlier than Saeman, Simha proposed another approach toward description of cellulose hydrolysis considering a variation of the molecular chain distribution. These depolymerisation models rely on random and nonrandom scission of long polymer chains [72]. Depolymerisation kinetics was investigated according to two aspects: (1) determination of all possible chain lengths distribution at different stages of the reaction; (2), changes of the average molecular weight with time. However, random scission has been assumed in many cases. The average degree of polymerization $\left(\overline{\mathrm{DP}}\right)$ was defined as follows (Eq. (5)):

$$\overline{\mathrm{DP}} = 1 - \exp(-\mathrm{kt}) \tag{5}$$

Here, $\overline{\mathrm{DP}}$ was the function of time since the start of the reaction [72]. The hydrolysis of cellulose was described best assuming the end bonds react twice as fast compared to internal glycosidic bonds [72].

In most depolymerisation studies, hydrolysis is characterised by the evolution of chain scissions determined via the change of the degree of polymerisation with time. A kinetic model derived from a first or pseudo-zero order Ekenstam's equation describes this behavior (Eq. (6)) [73,74]:

$$\frac{1}{\mathrm{DP}} - \frac{1}{\mathrm{DP_0}} = \mathrm{kt} \tag{6}$$

Therein, k denotes the reaction rate constant, DP_0 is the initial value of the degree of polymerisation and DP is the degree of polymerisation at a certain time *t*. These models were verified by experimental
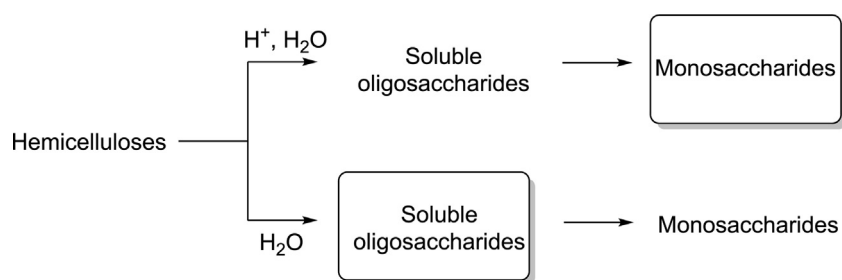
Fig. 4. Scheme of hemicelluloses hydrolysis: Monosaccharides are the major products under acid conditions; soluble oligosaccharides dominate in case of auto-hydrolysis.

Table 2
Literature data on apparent activation energies obtained for hydrolysis of cellulose.

Substrate	Temperature/°C	Acid concentration	E_a/kJ mol^{-1}	References
α-Cellulose	220–240	0.2–1 wt%	177	[78]
Kraft paper	180–240	0.2–1 wt%	188	[79]
Douglas fir	170–190	0.4–1 wt%	179	[29]
Solka-floc	180–240	0.5–2 wt%	177	[80]
Filter paper	200–240	0.4–1.5 wt%	178	[81]
Paper refuse	180–240	0.2–1 wt%	137	[79]
Municipal solid wastes	200–240	1.3–4.4 wt%	171	[36]
Sunflower residues	110–140	0.5–6 wt%	101	[82]
Hardwood	170–190	4.41–12.2 wt%	165	[83]
Microcrystalline cellulose	25–40	30–70 wt%	127	[31]
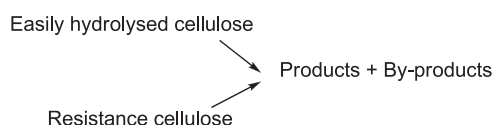
Fig. 5. Kinetic conventional model for cellulose hydrolysis including two fractions of cellulose [35].

Fig. 6. Conventional kinetic model for cellulose hydrolysis including modified cellulose. Reprinted with permission of American Chemical Society from Ref. [84].

Fig. 7. Conventional kinetic model for cellulose hydrolysis including a parasitic pathway. Depicted with kind permission from Springer Science + Business Media from Ref. [33].

data. However, since the scission of bonds is not easily determined, the degradation of polysaccharides is often studied by simple monitoring their weight loss [75,76].

Depolymerisation studies can utilize two different models: (1) a single-step first-order model considering glucose as sole product; (2) a multistep model taking the formation of intermediates into account, respectively. Since it is difficult to identify and quantify intermediates, a single-step first-order model was preferred in most studies. Therefore, several investigations suggested a single-step model of depolymerisation by considering the scission of glycosidic bonds releasing glucose to simulate the weight loss behavior during hydrolysis [75,77].

The yield of glucose produced by hydrolysis of cellulose is often not quantitative. Some attempts to explain this finding in the frame of simple kinetic models were made. For example, the kinetic model proposed by Saeman predicts only glucose yields up to 60–65% during acid hydrolysis of cellulose [29]. Conner et al. incorporated a reaction with two fractions of cellulose, one more easily hydrolysed than the other as well as further transformations of glucose into other products (Fig. 5). Overall, the degradation of glucose appears to be the major reason of limited glucose yields observed during acid hydrolysis [35].

Moreover, Bouchard et al. determined structural modifications of cellulosic solid substrates when applying two different conditions: (a) low temperature (100 °C) and high acid concentration and (b) high temperature (190 °C) and low acid concentration. Thermogravimetric analysis, differential scanning calorimetry, and FTIR were applied characterising partially hydrolysed cellulose. Formation of char in yields as high as 35% was reported. Based on these results, the authors suggested a new kinetic pathway for cellulose degradation facilitating the prediction of conversion and sugar yields (Fig. 6) [84].
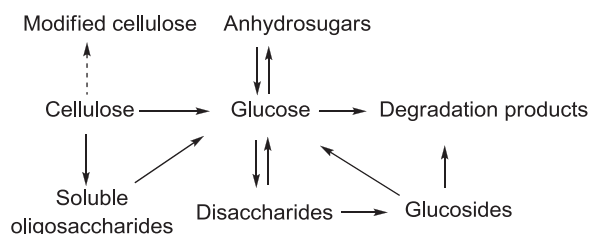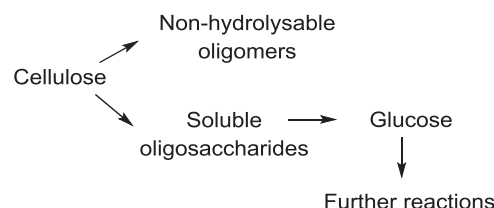
Interestingly, applying more diluted acid solutions (0.05 wt.%) and higher reaction temperature (215 °C), Mok et al. were able to avoid major structural changes of cellulose. However, under such conditions, the yield of glucose did not exceed 70%. They explained the limited yield by existence of a parasitic pathway. Hence, even in the absence of an acidic catalyst, cellulose partly converts into soluble products of unknown nature, which are not easily hydrolysed to glucose. In the presence of acids, this pathway competes with glucose formation. Based on these observations, another reaction network was suggested (Fig. 7) [33].

4.2. Hemicelluloses

As mentioned above, the first attempts to describe the kinetics of hemicelluloses hydrolysis were made using the Saeman model [85]. However, experimental data on acid pre-hydrolysis or aqueous
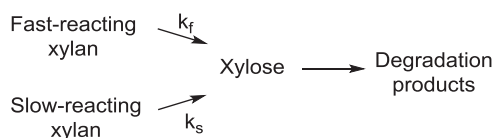
Fig. 8. Conventional biphasic model for xylan hydrolysis proposed by Kobayashi and Sakai, $k_f > k_s$ [40].

Fig. 9. Integration of xylose degradation into the conventional hydrolysis model improves the fitting [54].

hydrolysis of non-isolated hemicelluloses can be hardly described in terms of the Saeman model. As long ago as in 1955, Kobayashi and Sakai proposed an improved model for hydrolysis of xylan of hardwood [40], which could also be applied for hydrolysis of herbaceous xylan [43]. This approach is generally called a kinetic "biphasic model" as it includes a tentative separation of xylan into "fast-reacting xylan" and "slow-reacting xylan" (Fig. 8). Experimentally the presence of the two phases is reflected as an inflection point in the kinetic curve of xylan consumption.

Typically, the amounts of "fast-reacting xylan" and "slow-reacting xylan" are determined experimentally from kinetic data by means of best fitting [49]. Thus the part of "fast-reacting xylan" (denoted in literature as α) is 55 to 100% [40,43–45], the most frequently 70-80% [40,43,45]. α depends on the plant species [5,43,45] and reaction conditions such as temperature [5,44,46] and acid concentration [44]. Shen and Wyman have recently advocated the application of α as a characteristic of lignocellulosic materials that should not be affected by the reaction conditions. Therefore, it was proposed to determine "fast-reacting xylan" as a fraction of loosely bonded hemicelluloses that can be hydrolysed with water under mild conditions [49]. Alternatively, Lavarack et al. reported a procedure that includes treatment of the substrate by 4 wt.% H_2SO_4 at 90 °C resulting in hydrolysis of "fast-reacting xylan", whereas all the remaining xylan was referred to as "slow-reacting" [45,62]. The fundamental origin of the observed differences in reactivity of "fast-reacting xylan" and "slow-reacting xylan" has not been determined so far. The behavior has probably the following reasons (i) transport limitations; (ii) different portions of xylan have various intrinsic reactivity; (iii) the reaction occurs at a xylan-water interface and the rate is proportional to the changing interfacial area; (iv) fractions of xylan bonded and not-bonded with lignin have different reaction rates [5,46]. Definitely, detailed insights into the composition of lignocellulose are crucial to elucidate the observed differences in hydrolysis kinetics on a molecular level. Noteworthy, a recent study on acid hydrolysis of isolated xylan showed that its hydrolysis can be described in terms of a pseudo-first order model instead of a biphasic model [54]. Moreover, upon treatment of lignocellulose with water at high temperature, ca. 70% of xylan is recovered [49,57,60] which correlates with the part of "fast-reacting xylan" [40,43,45]. These data confirm that diffusion and/or chemical association with other components of lignocellulose clearly play an important role for the formation of "slow-reacting xylan". As mentioned above, some studies affirmed the simplest Saeman model to fit better than the "biphasic model" to describe acid pre-hydrolysis of lignocellulose. A potential explanation refers to hydrolysis of only "fast-reacting xylan", whereas "slow-reacting xylan" stays unhydrolysed [45,57].

The Saeman model and the biphasic model provide scarce information on the reaction evolution, as they do not consider intermediates. Nevertheless, even some results obtained by means of such simplifications support understanding of the reaction network. Especially, knowledge with regard to kinetics of accumulation and degradation of monosaccharides could be gained. A number of investigations showed that at pH lower than 2.0–2.5, kinetics of xylose accumulation becomes independent of the nature of acid used as catalyst [54]. Nevertheless, the stability of xylose proved to be higher in presence of maleic acid [53,54] compared
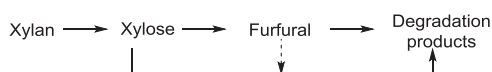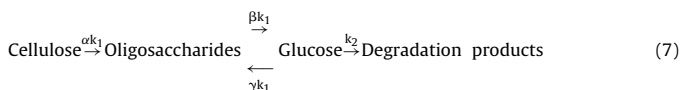
to sulfuric or oxalic acid. For instance, increasing the concentration of sulfuric acid causes an accelerated xylose decomposition. In contrast to this trend, a higher concentrated maleic acid solution stabilizes xylose slowing down its degradation [54]. One of the possible explanations of xylose stabilization by maleic acid is connected with the structural resemblance between the diacid and active sites of enzymes [53]. However, experimental evidence of this hypothesis is still required. Noteworthy, maleic acid possesses limited stability at high reaction temperatures, a fact that should be taken into account when considering such catalyst systems [54].

In general, a lot of attention was paid to monosaccharide decomposition with the major goal to suppress these undesired subsequent transformations (Section 3). Carbohydrates easily undergo degradation reactions ultimately forming humin side-products under acid conditions. However, little is known about the structure of these partly rehydrated polymeric compounds [86]. The primary kinetic models consider hydrolysis of xylan as a sequence of reactions comprehending (1) xylan hydrolysis to xylose, (2) dehydration of xylose into furfural, and (3) further degradation of furfural to humins. However, modeling of xylose decomposition using this model poorly fits experimental data. Taking into account the reaction between xylose and furfural as an alternative degradation pathway improves the fitting. Thus, a model based on a reaction network illustrated in Fig. 9 appears to be consistent with experimental data [54,87]. Moreover, investigations of the mechanism of monosaccharides degradation support the suggested route of humin formation [88].

5. Kinetic models considering oligosaccharides as intermediates

5.1. Cellulose

Since the first kinetic model proposed by Saeman, several modifications were added to include additional factors. The most recent model for diluted acid hydrolysis of cellulose includes the presence of soluble oligomeric intermediates which were found in non-negligible quantities during hydrolysis at high temperatures (>200 °C) and low acid concentrations (<1 wt.%). The conversion of oligomers to glucose is two to three times faster compared to hydrolysis of cellulose to soluble oligomers; therefore, oligomer formation was initially not recognized [78]. Abatzoglou et al. reported the presence of oligomers in significant amounts in the initial stages of diluted acid hydrolysis of cellulose. Therefore, the Saeman model was modified according to Eq. (7).

$$\text{Cellulose} \xrightarrow{\alpha k_1} \text{Oligosaccharides} \underset{\gamma k_1}{\overset{\beta k_1}{\rightleftarrows}} \text{Glucose} \xrightarrow{k_2} \text{Degradation products} \qquad (7)$$

In their proposed mechanism, three possibilities were considered: (1) the reaction of oligomers to glucose is in equilibrium; (2) the hydrolysis of oligomers to glucose is not in equilibrium; and (3) there are no repolymerisation reactions from glucose to oligomers. The third model was in agreement with experimental data. Abatzoglou et al. suggested two-step reactions in which hydrolysis of cellulose to oligomers appears in the first stage, followed by a further transformation of oligomers to glucose in the second stage under milder conditions.

Significant insights into the kinetics and mechanisms of the depolymerisation of linear polysaccharides have been achieved by advanced analytical methods such as gel permeation chromatography, which enabled determining molecular weight distributions.

Hydrolysis of amorphous cellulose in cotton-based paper was studied using gel permeation chromatography to obtain a more detailed picture of the course of reaction. The change of the molecular weight distribution during reaction indicated that hydrolysis proceeded in several stages: In stage I, amorphous chains are broken once causing a large decrease of the degree of polymerisation. Stage II includes another scission of amorphous chains placed in regions near to the end of the amorphous segments delivering free oligomers. During stage III, most hydrolysis occurs on very short segments.

The kinetic analysis of the hydrolysis rate of later stages of degradation appears difficult. Though the overall rate of hydrolysis seems to be constant, yet, the intact amorphous chains in the earliest stage undergo further degradation to free oligomers. However, kinetic analysis showed that hydrolysis of intact amorphous regions of cellulose is the slowest step and can be described by a first order reaction [89].

5.2. Hemicelluloses

In analogy to cellulose, inclusion of the intermediates into kinetic models was a further step toward clarifying the processes during hydrolysis of hemicelluloses. The simplest approaches use again a characterisation of remaining xylan [67] and analysis of oligomers by means of post-hydrolysis [48]. The procedure of post-hydrolysis includes treatment of soluble products with 4% H_2SO_4 at 121 °C for 1 h [48]. Under these conditions, oligomers undergo hydrolysis to monomers without subsequent decomposition; therefore, the total amount of soluble oligosaccharides can be determined. Post-hydrolysis is very important for closing mass-balances, especially for auto-hydrolysis that provides mainly oligomeric products. Moreover, data on post-hydrolysis significantly contribute to a fundamental understanding of the mechanism of polysaccharide hydrolysis.

Facilitated access to the side chains of hemicelluloses compared to the backbone was suggested causing a preferential hydrolysis of side groups of hemicelluloses [18,42,55,57,90]. Indeed, several studies report on faster release of arabinose attached as side residue compared to xylose from the backbone as well as acetic acid [42,46,57]. Reports on hydrolysis of arabinogalactan [24,25] and galactoglucomannan [55,90] highlight faster release of monosaccharides from side chains followed by hydrolysis of the backbone. Additionally to better access, the readiness to hydrolysis can be explained by bonding of side chains via α-glycosidic bonds, whereas the units of backbones are connected with each other by β-glycosidic bonds (Table 1). Facilitated hydrolysis of α-glycosidic linkages compared to β-glycosidic ones is well known [91]. Interestingly, no preferential release of acetyl side groups occurs. On the contrary, data on kinetic modeling rather support a random scission of acetylated xylans, at least at high temperature. E.g. applying a simple "biphasic model", Maloney et al. observed no preferential release of acetic acid compared to xylose when studying hydrolysis of xylan over H_2SO_4 at temperatures higher than 130 °C [41]. At lower temperatures, deacetylation of xylan was indeed faster than xylan removal, but the overall reaction rate was rather low [41]. Later on, Garrote et al. investigated auto-hydrolysis of xylan [57]. They concluded on preferential scission of polysaccharides to yield acetylated oligosaccharides rather than deacetylation of the main chain (Fig. 10) [57].

More recently, a careful analysis of oligosaccharidic intermediates was conducted for hydrolysis of O-acetyl galactoglucomannan over HCl at pH 1–3 by means of exclusion chromatography and MALDI-TOF-MS [92]. The exclusion chromatography provided information on average molar mass and molar mass distribution, whereas MALDI-TOF-MS enabled analysis of oligosaccharides with degree of polymerisation of 2–5. A linear relationship between

inversed weight-average molar mass (M_w) and depolymerisation time evidences random chain cleavage. Additionally, the results obtained by means of MALDI-TOF-MS supported the hypothesis on random cleavage of the bonds [92]. Later on, Kusema et al. confirmed a random bond scission of galactoglucomannan [55].

6. Oligosaccharides as model substrates

6.1. Cellulose

Kinetic studies with model compounds are performed with the aim to obtain more detailed kinetic information for optimizing the reaction condition and catalyst performance. In a work reported by Bobleter et al., cellobiose as model compound of cellulose was used to investigate the behavior of hydrothermal and diluted acid hydrolysis. The region of pH where acidic hydrolysis turns into hydrothermolysis was subject of special interest. This region was best analysed at relatively high temperatures (160–250 °C) and low concentrations of sulfuric acid (0.01 N). The experimental results suggested a first order kinetics [93]:

$$\text{Cellobiose} \xrightarrow{k_1} \text{Glucose} \xrightarrow{k_2} \text{Degradation products} \qquad (8)$$
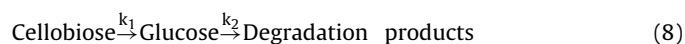
Interestingly, reaction rate constants for glucose formation and glucose degradation (k_1/k_2) had little dependency on temperature. At pH 2–3, the rate of hydrolysis was proportional to acid concentration. However, at pH 3–4.7 no influence of H_3O^+ concentration on the rate of hydrolysis could be observed. Additionally, the Zucker–Hammett plot for acid hydrolysis and hydrothermolysis showed a deviation of the hydrolysis rate in the pH range 3–4.7 indicating that hydrothermolysis follows a reaction mechanism different from acidic hydrolysis [93].

Another study compared hydrothermolysis of carbohydrates with their acidic hydrolysis. Hydrothermolysis of cellobiose in the range 180–249 °C was carried out. Kinetic analysis of the reaction showed that 60% of cellobiose was converted into glucose, and 40% into other products. The results indicated that, during hydrothermolysis, cellobiose is involved in at least one parallel reaction pathway to degradation products. Interpretation of the kinetic data pointed out that the hydrolysis of cellobiose to glucose is 50% higher than its conversion to degradation products [93].

Also Mosier et al. discussed acid hydrolysis of cellobiose with the aim to identify the optimum pH region for cellulose hydrolysis. Their results confirmed that acid catalysed hydrolysis is proportional to H_3O^+ concentration and varies for different acids. For example, carboxylic acids, i.e. maleic acid, did not catalyse the degradation of glucose while sulfuric acid did. Therefore, overall yields of glucose obtained from cellobiose and cellulose are higher in the presence of maleic acid compared to sulfuric acid at equivalent solution pH [28].

Kinetics of oligosaccharide hydrolysis was studied to gain insights into the rate of hydrolysis of different bond positions and the effects of chain length on the overall hydrolysis rate. In some studies, trimers were selected as model compounds. Freudenberg et al. investigated the rate of acid catalysed hydrolysis of cellotriose comparing the reactivity of glycosidic bonds during hydrolysis. In this study, the change in the reduction potential of the reaction mixture with time served as a measure of hydrolysis. The proposed reaction network is summarised in Fig. 11. Their study indicated equal specific rates of hydrolysis of two glycosidic bonds, which, however, differ from the rate of hydrolysis for cellobiose [94].

Feather and Harris utilized labeled cellotriose for elucidating the mechanism. Labeled cellotriose (cellotriose-1-^{14}C) was partially hydrolysed with sulfuric acid at 90 and 120 °C, respectively. The investigation pointed out that the glycosidic bond adjacent to the non-reducing end of cellotriose is hydrolysed about 1.5 times
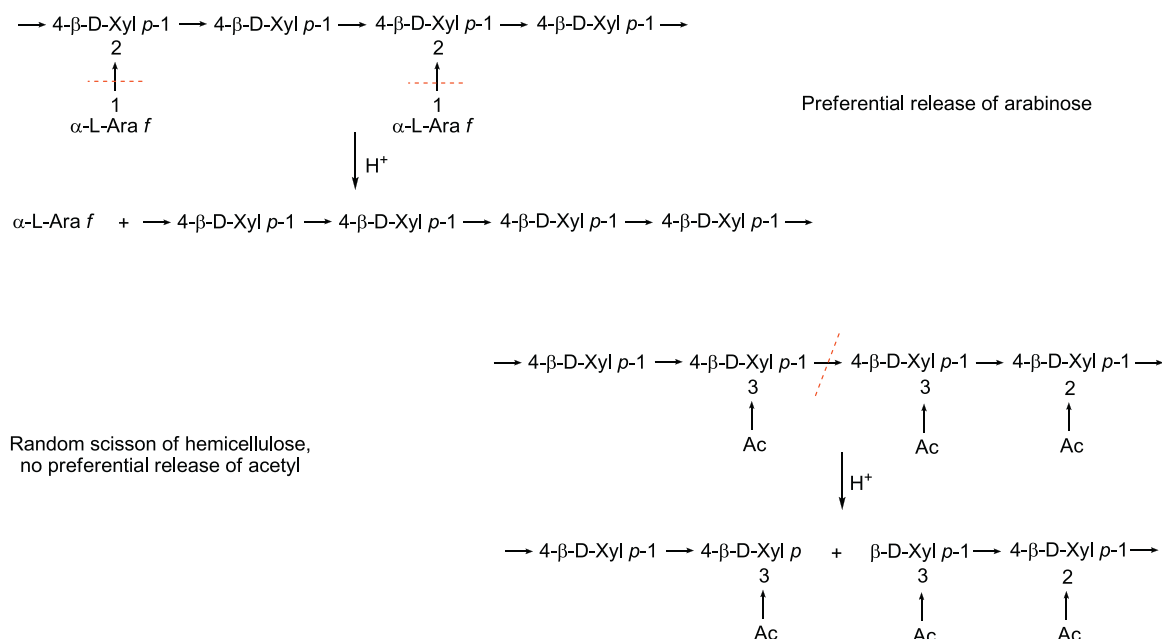
Fig. 10. Comparative rates of hydrolysis: (top) release of arabinose is quicker than hydrolysis of the xylan backbone [42,46,54], (bottom) whereas acetylated xylan undergoes random scission of the backbone [42,46,54]. The results obtained by analyzing oligosaccharides intermediates.
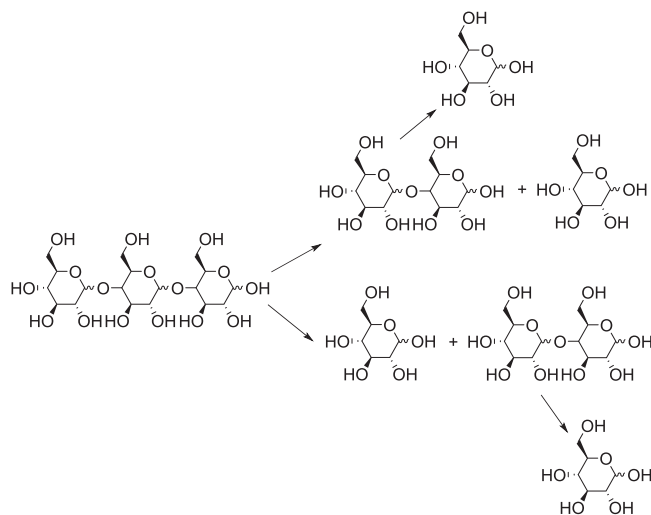
Fig. 11. Kinetic model for cellotriose hydrolysis as an example of using oligosaccharides as substrate. Reprinted from Ref. [94] with permission from Elsevier.

faster than the bond adjacent to the reducing end, and at a rate close to that of cellobiose [95]. Comparable results were obtained for hydrolysis of maltotriose and maltohexaose, that are oligosaccharides consisting of glycopyranosyls connected via an α(1->4) bond. Therein, the rate constant for hydrolysis of the non-reducing end of the chain was 1.8 times higher compared to the value for the other glycosidic bonds [96].

Amylose is a polymer comprising of glucose units linked via α(1->4) glycosidic bonds. Amylose was labeled either on the reducing or non-reducing end with D-glucose ^{14}C to determine the reactivity of different bonds. This study confirmed that the terminal bonds are preferentially hydrolysed and their rate of hydrolysis is faster [97].

Recently, cellobiose and cellotriose were chosen as model compounds of cellulose to investigate the hydrolysis-hydrogenation of cellulose. Under conditions of hydrolysis-hydrogenation, hydrolysis of cellooligomers competes with hydrogenation of their carbonyl functionality into an alcohol group. In most cases, hydrolysis is slower than the reduction. Interestingly, the rate of hydrolysis of the oligosaccharides after reduction is higher than of cellobiose and cellotriose [91,98]. Application of the oligosaccharides as substrates is easier in terms of analysis and usually allows access to well-elaborated kinetic models. However, the possibility to apply the knowledge obtained using a model system to real polymers is of utmost importance.

Monte Carlo approaches use the experimentally obtained data on kinetic constants developing models for hydrolysis of polymeric cellulose. The basis of this method is to construct a kinetic model based on probability, e.g. considering the reaction rate constants as "probabilities per unit time". Thus, depolymerisation in terms of scission of the chain will happen with a certain probability [99].
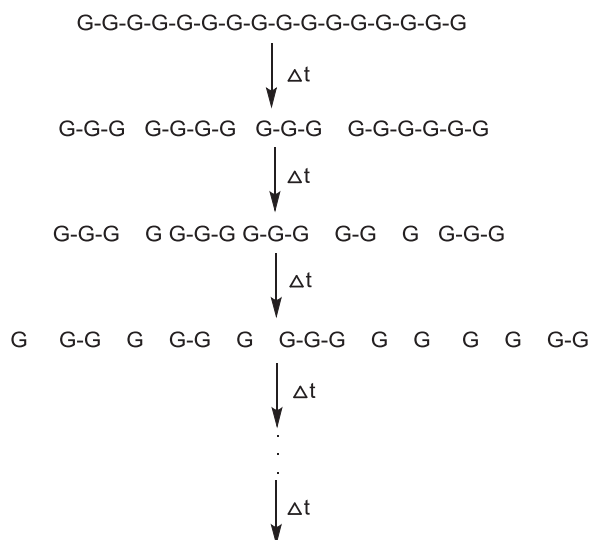
$$\text{Prob}_i = 1 - e^{k_i \Delta t} \quad i = 1, 2, \ldots \tag{9}$$

The polymer is considered as a Markov chain, a group of parallel sub-systems, each being composed of a single bond (Fig. 12). The course of depolymerisation in the Monte Carlo approach is predicted using kinetic information obtained from model compounds.

Different assumptions have been applied to the depolymerisation model of linear polysaccharides when using the Monte Carlo method such as: (1) the rate of cleavage is the same for all bonds and is independent of the position in the chain; (2) there is a preferential cleavage at the ends of the chain; (3) there is a progressive change in the rate of cleavage as a function of the distance from the ends of the chains [101,102].

Acid hydrolysis of glycosidic bonds in polysaccharides has been described by Monte Carlo methods. For example, a Monte Carlo procedure was developed simulating amylose depolymerisation using kinetic information obtained from cellobiose hydrolysis. The simulation permitted to foresee the time evolution of product distribution upon substrate depolymerisation [99].

Dadach et al. simulated the acid hydrolysis of cellulose at temperatures between 120 and 160 °C with sulfuric acid using a Monte Carlo method. For simulation, kinetic information related to hydrolysis of cellobiose and morphological aspects of cellulose including crystalline, semi-amorphous, and amorphous zones were considered. In the model both cleavage of a glycosidic bond and degradation of glucose were assumed to be two irreversible

G-G-G-G-G-G-G-G-G-G-G-G-G-G-G-G

↓ Δt

G-G-G   G-G-G-G   G-G-G   G-G-G-G-G-G

↓ Δt

G-G-G   G G-G-G G-G-G   G-G   G   G-G-G

↓ Δt

G   G-G   G   G-G   G   G-G-G   G   G   G   G   G-G

↓ Δt

⋮

↓ Δt

Fig. 12. Monte Carlo depolymerisation scheme; G (glucose unit), depicted from Ref. [100] with permission from Wiley-VCH. Experimental data obtained for oligosaccharides substrates were applied for modeling.

sequential reactions. The simulation indicated that for all temperatures, the overall glucose disappearance rate constant was higher than the experimental constant obtained from degradation of pure glucose. From the results, Dadach et al. concluded that the recombination of glucose with cellulose and oligomers is facilitated in the course of acid hydrolysis [100]. In general, successful modeling of hydrolysis of polysaccharides using the Monte Carlo method justifies application of oligosaccharides as model substrates for modeling the complex hydrolysis process.

6.2. Hemicelluloses

A number of studies included hemicellulosic oligosaccharides as substrates. Such reactions are usually considered as a further upgrading of a mixture of soluble oligomers obtained by autohydrolysis of hemicelluloses [18,54,103]. In order to improve fitting of experimental data to the kinetic model, Garrote et al. proposed an alternative reaction scheme (Fig. 13) [64]. The model differs from the conventional one by an additional degradation pathway of low-weight oligosaccharides to furfural. When omitting this step, the model underestimated the amount of synthesized furfural [64]. Noteworthy, the studies of Garrote et al. did not include an analysis of the molecular weights of oligosaccharides; moreover, the degrees of polymerisation of "high-weight" and "low-weight" oligosaccharides were not specified. Oligosaccharide concentrations were estimated based on kinetic data [57,60,64].

Later on, the dependency of oligosaccharide stability on the polymerisation degree was investigated in more details. Kumar et al. found out that xylobiose and xylotriose are not stable at 160 °C and degrade into unknown products [104]. The stability was studied at different pH values. Xylose proved to be the major product in acid media, but under neutral conditions the selectivity toward xylose decreases and decomposition dominates. No direct degradation of xylo-oligomers with polymerisation degrees of 4 and 5 was observed over a wide pH range of 1.45 to neutral [104].

A comprehensive study focusing on the rate of hydrolysis of xylo-oligosaccharides with a degree of polymerisation between 2 and 5 was conducted by Kamiyama and Sakai [105]. They demonstrated that all internal bonds as well as one terminal bond undergo hydrolysis at the same rate. Interestingly, one terminal glycosidic bond exhibits a 1.8 times faster rate of hydrolysis. However, kinetic modeling did not elucidate if accelerated hydrolysis occurs at the

reducing or non-reducing chain end [105]. A very recent study of Lau et al. targeted identifying the preferential depolymerisation route of oligosaccharides. Indeed, hydrolysis of xylose oligomers with a degree of polymerisation of 4 predominantly yields xylose and xylotriose under acidic conditions, but delivers two molecules of xylobioses in neutral medium [103]. Although a comprehensive mechanistical understanding of this observation is not available yet, it becomes obvious that in many cases a simple pseudo-first order model is too limited. Especially, studies aiming for a deeper understanding of predominant reaction pathways and overall reaction networks require insights with regard to major intermediate products.

7. Conclusion and outlook

Hydrolysis of cellulose and hemicelluloses is known for a long time. These processes present the starting points for upgrading of lignocellulosic biomass through platform molecules as feedstocks of chemical industry and biofuel production. Hydrolysis of polysaccharides is a complex transformation involving multiple reaction steps. Clearly, the sequence of reactions includes hydrolysis of polysaccharides to oligosaccharides followed by formation of monosaccharides and a potential subsequent further degradation. Nevertheless, very little is known about parallel and consecutive reactions taking place during hydrolysis. However, some aspects of the process have already been clarified by means of kinetic investigations.

Herein we reviewed the data on hydrolysis obtained in scopes of different kinetic approaches, namely (1) conventional models, (2) models considering oligosaccharides as intermediates, and (3) models utilizing oligosaccharides as substrates:

Conventional models generally focus on formation and degradation of monosaccharides only, without analyzing oligomeric intermediates. As a result, application of such approaches requires relatively simple analytical techniques such as HPLC or GC with preliminary derivatization of monosaccharides. An obvious disadvantage of the conventional models is poor information on reaction network and mechanisms. Nevertheless, even using the simplest conventional models provided some insights into the hydrolysis of cellulose and hemicelluloses. For instance, different rates of hydrolysis emphasized that xylan is embedded into lignocellulose in two different forms. Kinetic studies of cellulose hydrolysis provided information on the stability of cellulose against degradation, which is dependent on the reaction conditions.

Analysis of oligosaccharides as intermediates enables better understanding of hydrolysis processes. For example, the position of preferential cleavage within polysaccharide chains can be determined when tracing molecular-mass distribution of oligosaccharides during the reaction. Therein, significant differences between glycosidic bonds located in the main chain and the side chains of hemicelluloses were identified. Requirement for sophisticated analytical equipment, such as gel permeation chromatography or MALDI-TOF-MS, remains the main challenge for application of these very informative kinetic models.

Investigation of hydrolysis of oligosaccharides with defined molecular structures instead of a pool of poly- and oligosaccharides significantly facilitates kinetic and mechanistic studies. As a result, kinetic analysis of oligosaccharide hydrolysis provided detailed information on the rate of hydrolysis of different bond positions. For example, kinetic analysis of cellotriose showed that the glycosidic bond adjacent to the non-reducing end of cellotriose was hydrolysed faster than the bond adjacent to the reducing end. However, short oligosaccharides (under 10 repeating units) were utilized so far for kinetic modeling. Therefore, a question arises concerning applicability of these kinetic data to hydrolysis of polysaccharides consisting of up to thousands of repeating units. Nevertheless, some
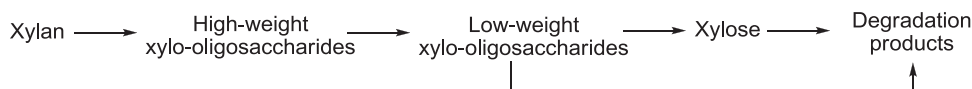
Fig. 13. Model of xylan hydrolysis including direct degradation of low-weight xylo-oligosaccharides proposed by Garrote et al. [54,60,64].

methods such as Monte Carlo have been applied for modeling of cellulose hydrolysis to enhance the understanding of these complex processes. In such methods, kinetic information of hydrolysis of simplest model compounds are used to predict the depolymerisation behavior of polysaccharides.

Certainly, detailed analysis of substrates, intermediates and products is required for comprehensive kinetic studies of polysaccharide hydrolysis. However, quantitative analysis of complex hydrolysates remains challenging and limits the development of more sophisticated kinetic models of hydrolysis. Nonetheless, with further progress of suitable analytical techniques for complex poly- , oligo- and monosaccharide mixtures kinetic modeling will clearly present a major tool elucidating dominant reaction pathways under various process conditions.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2015. 11.039.

References

[1] J. Geboers, S. Van de Vyver, R. Ooms, B. Op de Beeck, P.A. Jacobs, B.F. Sels, Chemocatalytic conversion of cellulose: opportunities, advances and pitfalls, Catal. Sci. Technol. 1 (2011) 714–726.

[2] G.W. Huber, S. Iborra, A. Corma, Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering, Chem. Rev. 106 (2006) 4044–4098.

[3] M.J. Climent, A. Corma, S. Iborra, Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels, Green Chem. 16 (2014) 516–547.

[4] I. Delidovich, K. Leonhard, R. Palkovits, Cellulose and hemicellulose valorisation: an integrated challenge of catalysis and reaction engineering, Energy Environ. Sci. 7 (2014) 2803–2830.

[5] F. Carrasco, C. Roy, Kinetic study of dilute-acid prehydrolysis of xylan-containing biomass, Wood Sci. Technol. 26 (1992) 189–208.

[6] F. Carvalheiro, L.C. Duarte, F.M. Gírio, Hemicellulose biorefineries: a review on biomass pretreatments, J. Sci. Ind. Res. 67 (2008) 849.

[7] N. Mosier, C. Wyman, B. Dale, R. Elander, Y.Y. Lee, M. Holtzapple, M. Ladisch, Features of promising technologies for pretreatment of lignocellulosic biomass, Bioresour. Technol. 96 (2005) 673–686.

[8] J.Q. Bond, A.A. Upadhye, H. Olcay, G.A. Tompsett, J. Jae, R. Xing, D.M. Alonso, D. Wang, T. Zhang, R. Kumar, A. Foster, S.M. Sen, C.T. Maravelias, R. Malina, S.R.H. Barrett, R. Lobo, C.E. Wyman, J.A. Dumesic, G.W. Huber, Production of renewable jet fuel range alkanes and commodity chemicals from integrated catalytic processing of biomass, Energy Environ. Sci. 7 (2014) 1500–1523.

[9] G.-Q. Chen, M.K. Patel, Plastics Derived from biological sources: present and future: a technical and environmental review, Chem. Rev. 112 (2011) 2082–2099.

[10] S. Jacobsen, C. Wyman, Cellulose and hemicellulose hydrolysis models for application to current and novel pretreatment processes, in: M. Finkelstein, B. Davison (Eds.), Twenty-First Symposium on Biotechnology for Fuels and Chemicals, Humana Press, 2000, pp. 81–96.

[11] C. Li, Z.K. Zhao, Efficient acid-catalyzed hydrolysis of cellulose in ionic liquid, Adv. Synth. Catal. 349 (2007) 1847–1850.

[12] C.E. Wyman, S.R. Decker, M.E. Himmel, J.W. Brady, C.E. Skopec, L. Viikari, Hydrolysis of Cellulose and Hemicellulose, in: Polysaccharides: Structural Diversity and Functional Versatility, 2nd ed., Marcel Dekker, New York, 2004, pp. 995–1033.

[13] M. Sasaki, B. Kabyemela, R. Malaluan, S. Hirose, N. Takeda, T. Adschiri, K. Arai, Cellulose hydrolysis in subcritical and supercritical water, J. Supercrit. Fluids 13 (1998) 261–268.

[14] M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri, K. Arai, Dissolution and hydrolysis of cellulose in subcritical and supercritical water, Ind. Eng. Chem. Res. 39 (2000) 2883–2890.

[15] P. Mäki-Arvela, T. Salmi, B. Holmbom, S. Willför, D.Y. Murzin, Synthesis of sugars by hydrolysis of hemicelluloses—a review, Chem. Rev. 111 (2011) 5638–5666.

[16] Y. Lee, P. Iyer, R. Torget, G. Tsao, Dilute-Acid Hydrolysis of Lignocellulosic Biomass Recent Progress in Bioconversion of Lignocellulosics, Springer, Berlin Heidelberg, 1999, pp. 93–115.

[17] Y.-B. Huang, Y. Fu, Hydrolysis of cellulose to glucose by solid acid catalysts, Green Chem. 15 (2013) 1095–1111.

[18] L. Vilcocq, P.C. Castilho, F. Carvalheiro, L.C. Duarte, Hydrolysis of oligosaccharides over solid acid catalysts: a review, ChemSusChem 7 (2014) 1010–1019.

[19] S. Dumitriu, Polysaccharides: structural diversity and functional versatility, 2nd ed, Marcel Dekker, New York, 2005.

[20] D. Klemm, B., Heublein, H.P., Fink, A., Bohn, Cellulose Fascinating biopolymer and sustainable raw material, Angewandte Chemie–International Edition, 44 (2005) 3358–3393.

[21] C.J.A. Vinkx, J.A. Delcour, Rye (*Secale cereale* L.) arabinoxylans: a critical review, J. Cereal Sci. 24 (1996) 1–14.

[22] T.E. Timell, Recent progress in the chemistry of wood hemicelluloses, Wood Sci. Technol. 1 (1967) 45–70.

[23] A. Ebringerová, Z. Hromádková, T. Heinze, Hemicellulose, in: T. Heinze (Ed.), Polysaccharides I, Springer, Berlin Heidelberg, 2005, pp. 1–67.

[24] B.T. Kusema, C. Xu, P. Mäki-Arvela, S. Willför, B. Holmbom, T. Salmi, D.Y. Murzin, Kinetics of acid hydrolysis of arabinogalactans, Int. J. Chem. React. Eng. 8 (2010) 18–41, A44.

[25] B.T. Kusema, G. Hilmann, P. Mäki-Arvela, S. Willför, B. Holmbom, T. Salmi, D.Y. Murzin, Selective hydrolysis of arabinogalactan into arabinose and galactose over heterogeneous catalysts, Catal. Lett. 141 (2011) 408–412.

[26] K. Bunnell, A. Rich, C. Luckett, Y.-J. Wang, E. Martin, D.J. Carrier, Plant maturity effects on the physicochemical properties and dilute acid hydrolysis of switchgrass (*Panicum virgatum*, L.) Hemicelluloses, ACS Sus. Chem. Eng. 1 (2013) 649–654.

[27] J. Kim, Y.Y. Lee, R. Torget, Cellulose hydrolysis under extremely low sulfuric acid and high-temperature conditions, Appl. Biochem. Biotechnol. 91–93 (2001) 331–340.

[28] N.S. Mosier, C.M. Ladisch, M.R. Ladisch, Characterization of acid catalytic domains for cellulose hydrolysis and glucose degradation, Biotechnol. Bioeng. 79 (2002) 610–618.

[29] J.F. Saeman, Kinetics of wood saccharification—hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature, Ind. Eng. Chem. 37 (1945) 43–52.

[30] R. Aguilar, J.A. Ramírez, G. Garrote, M. Vázquez, Kinetic study of the acid hydrolysis of sugar cane bagasse, J Food Eng. 55 (2002) 309–318.

[31] F. Camacho, P. González-Tello, E. Jurado, A. Robles, Microcrystalline-cellulose hydrolysis with concentrated sulphuric acid, J. Chem. Technol. Biotechnol. 67 (1996) 350–356.

[32] A. Esteghlalian, A.G. Hashimoto, J.J. Fenske, M.H. Penner, Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover, poplar and switchgrass, Bioresour. Technol. 59 (1997) 129–136.

[33] J. Bouchard, G. Garnier, P. Vidal, E. Chornet, R.P. Overend, Characterization of depolymerized cellulosic residues, Wood Sci. Technol. 24 (1990) 159–169.

[34] D.R. Cahela, Y.Y. Lee, R.P. Chambers, Modeling of percolation process in hemicellulose hydrolysis, Biotechnol. Bioeng. 25 (1983) 3–17.

[35] A.H. Conner, B.F. Wood, C.G. Hill, J.F. Harris, Kinetic model for the dilute sulfuric acid saccharification of lignocellulose, J. Wood Chem. Technol. 5 (1985) 461–489.

[36] I.A. Malester, M. Green, G. Shelef, Kinetics of dilute acid hydrolysis of cellulose originating from municipal solid wastes, Ind. Engin. Chem. Res. 31 (1992) 1998–2003.

[37] Q. Qing, B. Yang, C.E. Wyman, Bioresour. Technol. 101 (2010) 9624–9630.

[38] Y. Kim, E. Ximenes, N.S. Mosier, M.R. Ladisch, Enzyme Microb. Technol. 48 (2011) 408–415.

[39] E. Ximenes, Y. Kim, N. Mosier, B. Dien, M. Ladisch, Enzyme Microb. Technol. 46 (2010) 170–176.

[40] T. Kobayashi, Y. Sakai, Hydrolysis rate of pentosan of hardwood in dilute sulfuric acid, Bull. Agric. Chem. Soc. Jpn. 20 (1956) 1–7.

[41] M.T. Maloney, T.W. Chapman, A.J. Baker, Dilute acid hydrolysis of paper birch: kinetics studies of xylan and acetyl-group hydrolysis, Biotechnol. Bioeng. 27 (1985) 355–361.

[42] G. González, J. López-Santín, G. Caminal, C. Solà, Dilute acid hydrolysis of wheat straw hemicellulose at moderate temperature: a simplified kinetic model, Biotechnol. Bioeng. 28 (1986) 288–293.

[43] A. Esteghlalian, A.G. Hashimoto, J.J. Fenske, M.H. Penner, Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover, poplar and switchgrass, Bioresour. Technol. 59 (1997) 129–136.

[44] R. Aguilar, J.A. Ramírez, G. Garrote, M. Vázquez, Kinetic study of the acid hydrolysis of sugar cane bagasse, J. Food Eng. 55 (2002) 309–318.

[45] B.P. Lavarack, G.J. Griffin, D. Rodman, The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose, arabinose, glucose and other products, Biomass Bioenergy 23 (2002) 367–380.

[46] A. Rodríguez-Chong, J. Alberto Ramírez, G. Garrote, M. Vázquez, Hydrolysis of sugar cane bagasse using nitric acid: a kinetic assessment, J. Food Eng. 61 (2004) 143–152.

[47] J. Jensen, J. Morinelly, A. Aglan, A. Mix, D.R. Shonnard, Kinetic characterization of biomass dilute sulfuric acid hydrolysis: mixtures of hardwoods, softwood, and switchgrass, AIChE J. 54 (2008) 1637–1645.

[48] J.E. Morinelly, J.R. Jensen, M. Browne, T.B. Co, D.R. Shonnard, Kinetic characterization of xylose monomer and oligomer concentrations during dilute acid pretreatment of lignocellulosic biomass from forests and switchgrass, Ind. Eng. Chem. Res. 48 (2009) 9877–9884.

[49] J. Shen, C.E. Wyman, A novel mechanism and kinetic model to explain enhanced xylose yields from dilute sulfuric acid compared to hydrothermal pretreatment of corn stover, Bioresour. Technol. 102 (2011) 9111–9120.

[50] I.S.M. Rafiqul, A.M. Mimi Sakinah, Kinetic studies on acid hydrolysis of Meranti wood sawdust for xylose production, Chem. Eng. Sci. 71 (2012) 431–437.

[51] G. Marcotullio, E. Krisanti, J. Giuntoli, W. de Jong, Selective production of hemicellulose-derived carbohydrates from wheat straw using dilute HCl or FeCl3 solutions under mild conditions. X-ray and thermo-gravimetric analysis of the solid residues, Bioresour. Technol. 102 (2011) 5917–5923.

[52] S. Gámez, J.J. González-Cabriales, J.A. Ramírez, G. Garrote, M. Vázquez, Study of the hydrolysis of sugar cane bagasse using phosphoric acid, J. Food Eng. 74 (2006) 78–88.

[53] Y. Lu, N.S. Mosier, Biomimetic catalysis for hemicellulose hydrolysis in corn stover, Biotechnol. Prog. 23 (2007) 116–123.

[54] Y. Kim, T. Kreke, M.R. Ladisch, Reaction mechanisms and kinetics of xylo-oligosaccharide hydrolysis by dicarboxylic acids, AIChE J. 59 (2013) 188–199.

[55] B.T. Kusema, T. Tönnov, P. Mäki-Arvela, T. Salmi, S. Willför, B. Holmbom, D.Y. Murzin, Acid hydrolysis of O-acetyl-galactoglucomannan, Catal. Sci. Technol. 3 (2013) 116–122.

[56] J. Xu, M.H. Thomsen, A.B. Thomsen, Recovery of arabinan in acetic acid-catalyzed hydrothermal pretreatment on corn stover, Biomass Bioenerg. 33 (2009) 1660–1663.

[57] G. Garrote, H. Domínguez, J.C. Parajó, Mild autohydrolysis: an environmentally friendly technology for xylooligosaccharide production from wood, J. Chem. Technol. Biotechnol. 74 (1999) 1101–1109.

[58] T. Lloyd, C.E. Wyman, Appl. Biochem. Biotechnol. 115 (2004) 1013–1022.

[59] D.R. Cahela, Y.Y. Lee, R.P. Chambers, Modeling of percolation process in hemicellulose hydrolysis, Biotechnol. Bioeng. 25 (1983) 3–17.

[60] G. Garrote, H. Domínguez, J.C. Parajó, Autohydrolysis of corncob: study of non-isothermal operation for xylooligosaccharide production, J. Food Eng. 52 (2002) 211–218.

[61] X. Liu, M. Lu, N. Ai, F. Yu, J. Ji, Kinetic model analysis of dilute sulfuric acid-catalyzed hemicellulose hydrolysis in sweet sorghum bagasse for xylose production, Ind. Crop. Prod. 38 (2012) 81–86.

[62] B.P. Lavarack, G.J. Griffin, D. Rodman, Measured kinetics of the acid-catalysed hydrolysis of sugar cane bagasse to produce xylose, Catal. Today 63 (2000) 257–265.

[63] X. Li, A. Converse, C. Wyman, Characterization of molecular weight distribution of oligomers from autocatalyzed batch hydrolysis of xylan, Appl. Biochem. Biotechnol. 107 (2003) 515–522.

[64] G. Garrote, H. Domínguez, J.C. Parajó, Kinetic modelling of corncob autohydrolysis, Process Biochem. 36 (2001) 571–578.

[65] R. Aguilar, J.A. Ramírez, G. Garrote, M. Vázquez, J. Food Eng. 55 (2002) 309–318.

[66] Y. Kim, R. Hendrickson, N. Mosier, M. Ladisch, Liquid Hot Water Pretreat-ment of Cellulosic Biomas, in: J.R. Mielenz (Ed.), Biofuels, Humana Press, 2009, pp. 93–102.

[67] D. Nabarlatz, X. Farriol, D. Montané, Kinetic Modeling of the Autohydrolysis of Lignocellulosic Biomass for the Production of Hemicellulose-Derived Oligosaccharides, Ind. Eng. Chem. Res. 43 (2004) 4124–4131.

[68] F. Carvalheiro, G. Garrote, J.C. Parajó, H. Pereira, F.M. Gírio, Kinetic modeling of breweryapos;s spent grain autohydrolysis, Biotechnol. Prog. 21 (2005) 233–243.

[69] W.L. Marshall, E.U. Franck, Ion product of water substance0–1000 (C, 1–10,000 bars New International Formulation and its background, J. Phys. Chem. Ref. Data 10 (1981) 295–304.

[70] C. Pronyk, G. Mazza, Kinetic modeling of hemicellulose hydrolysis from triticale straw in a pressurized low polarity water flow-through reactor, Ind. Eng. Chem. Res. 49 (2010) 6367–6375.

[71] Q. Xiang, Y.Y. Lee, P. Pettersson, R. Torget, Heterogeneous Aspects of Acid Hydrolysis of α-Cellulose, in: B. Davison, J. Lee, M. Finkelstein, J. McMillan (Eds.), Biotechnology for Fuels and Chemicals, Humana Press, 2003, pp. 505–514.

[72] R. Simha, Kinetics of degradation and size distribution of long chain polymers, J. Appl. Phys. 12 (1941) 569–578.

[73] P. Calvini, A. Gorassini, A. Merlani, On the kinetics of cellulose degradation: looking beyond the pseudo zero order rate equation, Cellulose 15 (2008) 193–203.

[74] H.Z. Ding, Z.D. Wang, On the degradation evolution equations of cellulose, Cellulose 15 (2008) 205–224.

[75] V. Mamleev, S. Bourbigot, M. Le Bras, J. Yvon, J. Lefebvre, Model-free method for evaluation of activation energies in modulated thermogravimetry and analysis of cellulose decomposition, Chem. Eng. Sci. 61 (2006) 1276–1292.

[76] D.K. Shen, S. Gu, The mechanism for thermal decomposition of cellulose and its main products, Bioresour. Technol. 100 (2009) 6496–6504.

[77] A.G.W. Bradbury, Y. Sakai, F. Shafizadeh, A kinetic model for pyrolysis of cellulose, J. Appl. Polym. Sci. 23 (1979) 3271–3280.

[78] N. Abatzoglov, J. Bouchard, E. Chornet, R.P. Overend, Dilute acid depolymerization of cellulose in aqueous phase: Experimental evidence of the significant presence of soluble oligomeric intermediates, Can. J. Chem. Eng. 64 (1986) 781–786.

[79] R.D. Fagan, H.E. Grethlei, A.O. Converse, A. Porteous, Kinetics of Acid Hydrolysis of Cellulose Found in Paper Refuse, Environ. Sci. Technol. 5 (1971) 545.

[80] D.R. Thompson, H.E. Grethlein, Design and evaluation of a plug flow reactor for acid-hydrolysis of cellulose, Ind. Eng. Chem. Prod. Res. Dev. 18 (1979) 166–169.

[81] J.P. Franzidis, A. Porteous, J. Anderson, The acid-hydrolysis of cellulose in refuse in a continuous reactor, Conserv. Recycl. 5 (1982) 215–225.

[82] L. Jiménez, J.L. Bonilla, Acid hydrolysis of sunflower residue biomass, Process Biochem. 28 (1993) 243–247.

[83] S.K. Song, Y.Y. Lee, Acid hydrolysis of wood cellulose under low water condition, Biomass 6 (1984) 93–100.

[84] W.S. Mok, M.J. Antal, G. Varhegyi, Productive and parasitic pathways in dilute acid-catalyzed hydrolysis of cellulose, Ind. Eng. Chem. Res. 31 (1992) 94–100.

[85] J.F. Saeman, Kinetics of wood saccharification - hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature, Ind. Eng. Chem. 37 (1945) 43–52.

[86] I. van Zandvoort, Y. Wang, C.B. Rasrendra, E.R.H. van Eck, P.C.A. Bruijnincx, H.J. Heeres, B.M. Weckhuysen, Formation molecular structure, and morphology of humins in biomass conversion: influence of feedstock and processing conditions, ChemSusChem 6 (2013) 1745–1758.

[87] R. Weingarten, J. Cho, J.W.C. Conner, G.W. Huber, Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating, Green Chem. 12 (2010) 1423–1429.

[88] S.K.R. Patil, C.R.F. Lund, Formation and growth of humins via aldol addition and condensation during acid-catalyzed conversion of 5-Hydroxymethylfurfural, Energy Fuels 25 (2011) 4745–4755.

[89] C.H. Stephens, P.M. Whitmore, H.R. Morris, M.E. Bier, Hydrolysis of the amorphous cellulose in cotton-based paper, Biomacromolecules 9 (2008) 1093–1099.

[90] T. Salmi, D.Y. Murzin, P. Mäki-Arvela, B. Kusema, B. Holmbom, S. Willför, J. Wärnå, Kinetic modeling of hemicellulose hydrolysis in the presence of homogeneous and heterogeneous catalysts, AIChE J. 60 (2014) 1066–1077.

[91] L. Negahdar, J.U. Oltmanns, S. Palkovits, R. Palkovits, Kinetic investigation of the catalytic conversion of cellobiose to sorbitol, Appl. Catal. B: Environ. 147 (2014) 677–683.

[92] C. Xu, A. Pranovich, L. Vähäsalo, J. Hemming, B. Holmbom, H.A. Schols, S. Willför, Kinetics of acid hydrolysis of water-soluble spruce O-acetyl galactoglucomannans, J. Agric. Food Chem. 56 (2008) 2429–2435.

[93] O. Bobleter, W. Schwald, R. Concin, H. Binder, Hydrolysis of cellobiose in dilute sulfuric-acid and under hydrothermal conditions, J. Carbohydr. Chem. 5 (1986) 387–399.

[94] K. Freudenberg, Hydrolysis and optical rotation of cellulose, starch, and cycloglucans, J. Polym. Sci. 23 (1957) 791–799.

[95] M.S. Feather, J.F. Harris, Partial hydrolysis and acetolysis of cellotriose-1-14C, J. Am. Chemi. Soc. 89 (1967) 5661–5664.

[96] M.S. Weintraub, D. French, Acid hydrolysis of $(1{\rightarrow}4)$-α -d-glucans: Part II. Analysis of products from radioactive oligosaccharides, Carbohydr. Res. 15 (1970) 251–262.

[97] J. Holló, E. László, J. Szejtli, G. Zala, Studien óber die saure Hydrolyse von Glykosidbindungen. IX Mitteilung: Hydrolyse der am reduzierenden und nicht reduzierenden Ende markierten Amylose, Starch-Stárke 16 (1964) 211–214.

[98] L. Negahdar, P.J.C. Hausoul, S. Palkovits, R. Palkovits, Direct cleavage of sorbitol from oligosaccharides via a sequential hydrogenation-hydrolysis pathway, Appl. Catal. B: Environ. 166–167 (2015) 460–464.

[99] J.-H.Q. Pinto, S. Kaliaguine, A Monte Carlo analysis of acid hydrolysis of glycosidic bonds in polysaccharides, AIChE J. 37 (1991) 905–914.

[100] D. Zin-Eddine, P.Q. José-Henrjque, S. Kaliaguine, Acid hydrolysis of cellulose. part ii: Stochastic simulation using a monte carlo technique, Can. J. Chem. Eng. 72 (1994) 106–112.

[101] T. Salmi, D.Y. Murzin, J.P. Mikkola, J. Warna, P. Maki-Arvela, E. Toukoniitty, S. Toppinen, Advanced kinetic concepts and experimental methods for catalytic three-phase processes, Ind. Eng. Chem. Res. 43 (2004) 4540–4550.

[102] J.N. Bemiller, Acid-Catalyzed Hydrolysis of Glycosides, in: L.W. Melville, R.S. Tipson (Eds.), Advances in Carbohydrate Chemistry, Academic Press, 1967, pp. 25–108.

[103] C.-S. Lau, G.J. Thoma, E.C. Clausen, D.J. Carrier, Kinetic modeling of xylose oligomer degradation during pretreatment in dilute acid or in water, Ind. Eng. Chem. Res. 53 (2014) 2219–2228.

[104] R. Kumar, C.E. Wyman, The impact of dilute sulfuric acid on the selectivity of xylooligomer depolymerization to monomers, Carbohydr. Res. 343 (2008) 290–300.

[105] Y. Kamiyama, Y. Sakai, Rate of hydrolysis of xylo-oligosaccharides in dilute sulfuric acid, Carbohydr. Res. 73 (1979) 151–158.